⑲ ⓒⒶ CANADIAN PATENT

� PRODUCTION OF CHLORINE DIOXIDE

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REMPLACEMENT

SECTION is not Present

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This invention relates to the production of chlorine dioxide.

Chlorine dioxide is utilized in a variety of bleaching operations, particularly in the bleaching of cellulosic fibrous material, such as, wood pulp produced by the Kraft and sulfite processes.

Chlorine dioxide is known to be prepared in a variety of ways, involving the reduction of an alkali metal chlorate, generally sodium chlorate, in an acid solution utilizing sulphur dioxide, sulphuric acid, chromic sulphate, methanol, sodium
10 chloride or hydrochloric acid as reducing agents. The basic reaction in all such processes is that between chlorate and chloride in the acid solution to produce chlorine dioxide, chlorine and water, in accordance with the equation:

$$2H^+ + ClO_3^- + Cl^- \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O$$
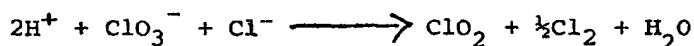
When sodium chloride or hydrochloric acid is the reducing agent, then chlorine is produced along with the chlorine dioxide. In the presence of other reducing agents, part of the chlorine is reduced to chloride in the reacting solution so that the chlorine dioxide produced contains lesser amounts of chlorine.

20 The acid medium may be provided by sulphuric acid where the reducing agent is sodium chloride, and may be provided both by sulphuric acid and hydrochloric acid where the reducing agent is hydrogen chloride. The acid medium may be wholly provided by hydrogen chloride also acting as the reducing agent.

In Canadian Patent 825,084, there is described a process of forming chlorine dioxide and chlorine from an alkali metal chlorate, an alkali metal chloride or hydrogen chloride

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or mixtures thereof, and sulphuric acid, in which chlorine dioxide and chlorine are generated and an alkali metal acid sulphate is crystallized in the same reaction zone. Water is evaporated from the reaction medium to remove the chlorine dioxide and chlorine from the reaction zone.

The alkali metal usually is sodium and the form of the acid sulphate product is dependent on the temperature and acidity of the reaction medium. At high acidities around 10 to 12 N and at temperatures of around 75 to 100°C, the sodium acid sulphate is in the form of sodium bisulphate ($NaHSO_4$). The reaction involved is represented by the equation:

$$NaClO_3 + NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + ClO_2 + \tfrac{1}{2}Cl_2 + H_2O.$$
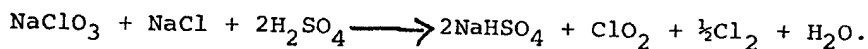
At lower acidities, around 5 to 9 N and lower temperatures of around 30° to 70°C, sodium sequisulphate ($Na_3H(SO_4)_2$) is formed. The reaction involved is represented by the equation:

$$3NaClO_3 + 3NaCl + 4H_2SO_4 \longrightarrow 3ClO_2 + \tfrac{3}{2}ClO_2 + 3H_2O + 2Na_3H(SO_4)_2.$$
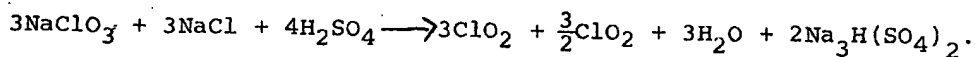
In Canadian Patent 826,577, there is described a process of preparing chlorine dioxide and chlorine by reacting sodium chlorate, sodium chloride and sulphuric acid under conditions of low acidity, generally of the order of 2 to 4.8 N. This process may be performed in a single reaction zone in accordance with the process of the above-mentioned Canadian Patent 825,084, evaporating water from the reaction medium to remove the chlorine dioxide and chlorine, and generally precipitating anhydrous sodium sulphate (Na_2SO_4) in the reaction zone.

The reaction involved in this latter process is represented by the following equation:

$$NaClO_3 + NaCl + H_2SO_4 \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O + Na_2SO_4$$
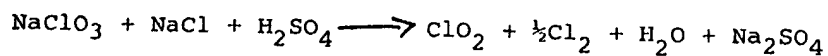
In all the above-described reactions there is a competing reaction in which no chlorine dioxide is formed represented by the equation:

$$NaClO_3 + 5NaCl + 3H_2SO_4 \longrightarrow 3Cl_2 + 3Na_2SO_4 + 3H_2O.$$
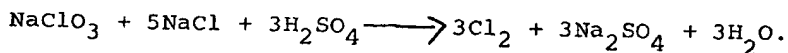
This reaction becomes significant when the mole ratio of chloride to chlorate in the reactor feed substantially exceeds 1:1. In order to maximize production of chlorine dioxide from chlorate, it is preferred to operate the above process at approximately equimolar or slightly higher molar ratio of chloride to chlorate in the feed.

Another process for the production of chlorine dioxide is described in Canadian Patent No. 913,328 in which hydrochloric acid forms the acid medium and the reducing agent. The process, when sodium chlorate is reduced, is represented by the equation:

$$NaClO_3 + 2HCl \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O.$$
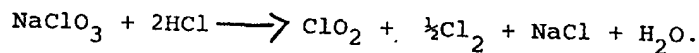
In the processes described in the above-mentioned Canadian patents, the evaporation is carried out at the boiling point of the reaction medium under a reduced pressure to deposit product alkali metal sulphate or alkali metal chloride in the reactor and the liquid level in the vessel generally is maintained at a substantially constant level by balancing the water added with that evaporated. The evaporated water acts as diluent gas for the generated chlorine dioxide and chlorine and removes the gaseous products from the reaction vessel.

The present invention is directed to chlorine dioxide processes in which water is evaporated from the reaction vessel to act as diluent for the chlorine dioxide and in which solid alkali metal salt is deposited in the reaction zone.

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Preferably, the process is one of those described in the above-mentioned Canadian Patents 825,084; 826,577 and 913,328.

The reaction vessel may be of any convenient design and usually includes a cylindrical body with a conical base. A conduit for removal from the vessel of solid product in a slurry with some reaction medium communicates with the conical base. Solid material is removed from the slurry and make-up chemicals are added to the remaining material before recycle to the reaction vessel. The recycling liquid is heated in a heat exchanger, typically to substantially the boiling temperature of the solution under the prevailing conditions of the reaction vessel, prior to discharge to the reaction vessel.

The process of the invention is described hereinafter particularly with reference to reduction of an alkali metal chlorate with an alkali metal chloride or a mixture of an alkali metal chloride and hydrogen chloride in a sulphuric acid containing medium. Preferably, the alkali metal chlorate is sodium chlorate and the alkali metal chloride is sodium chloride.

In conventional evaporator practice in which a liquid is evaporated in a vessel, a slurry is removed, solid is recovered and liquid is recycled and reboiled during recycle, the liquid is prevented from boiling in the recycle line by operating the vessel with the level of liquid above the entry point of the recycled liquid a height greater in hydrostatic head than the increase in saturated vapour pressure caused by the temperature rise across the recycle loop heater.

However, in the chlorine dioxide-producing processes
used in the present invention, since there is reaction to
form chlorine dioxide upon addition of sulphuric acid to the
recycling chemicals in the recycle loop it is not possible
to have the level of liquid in the reaction vessel above the
discharge point of the recycled liquid. The recycled material
therefore is discharged above the level of the liquid in the
reaction vessel.

The velocity of the liquid in the recycle loop and
10   discharging to the reaction vessel above the liquid level
therein must be maintained above a predetermined minimum value
to prevent boiling of the liquid in the heat exchanger and
to prevent vibration due to flashing flow acceleration. This
minimum velocity is high and as a result the discharging
material may impinge on the opposite wall of the vessel.
Due to the solids content of this material, the vessel wall
is subject to wear by the impinging material.

The present invention is concerned with modifying
the recycle operation in order to avoid wear to the vessel
20   walls, while at the same time achieving satisfactory recycle
and reaction efficiency. In the present invention, boiling
in the liquid from the recycle loop heater is allowed to develop
gradually while maintaining acceleration at a low level, prior
to discharge to the reaction vessel. In this way, it is poss-
ible to discharge recycled material to the reaction vessel
at low velocity while vibration due to flashing flow acceler-
ation is minimized.

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In accordance with one aspect of the present invention, there is provided a continuous method of producing chlorine dioxide which comprises continuously maintaining a chlorine dioxide-producing reaction medium in a reaction zone, the reaction medium containing an alkali metal chlorate, a reducing agent capable of reducing the alkali metal chlorate to chlorine dioxide and chlorine and a strong mineral acid, continuously generating chlorine dioxide and chlorine from the reaction medium and continuously evaporating water from the

10 reaction medium at substantially the boiling point thereof while the reaction medium is maintained under a reduced pressure, continuously removing from the reaction zone a gaseous mixture consisting of the generated chlorine dioxide and chlorine and the evaporated water, continuously recovering chlorine dioxide from the gaseous mixture, continuously depositing in the reaction zone an alkali metal salt of the anion of the strong acid, continuously removing from the reaction zone a slurry containing deposited alkali metal salt and part of the reaction medium, continuously forming a recycle mixture having

20 a reduced alkali metal salt solids content and containing make-up quantities of alkali metal chlorate and reducing agent, except that the reducing agent is omitted from the recycle mixture when the strong mineral acid also provides the reducing agent, heating the recycle mixture substantially to an elevated temperature which is the boiling point of the reaction medium at the prevailing absolute pressure in the reaction zone, accelerating the heated mixture to establish a back pressure exceeding the difference in saturation vapour pressure of the heated mixture and of the reaction medium,

30 adding strong mineral acid to the accelerated heated mixture substantially at the maximum velocity of the mixture resulting from the acceleration to provide a feed material for the reaction zone, allowing gaseous material in the feed material

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to expand while maintaining a low rate of acceleration, feeding the expanded feed mixture to the reaction zone at a level above the liquid level in the reaction zone and maintaining the level of liquid in the reaction zone substantially constant.

In accordance with a further aspect of the present invention, there is provided in a gaseous reaction product generator comprising a reaction vessel adapted to hold an aqueous reaction medium and capable of forming gaseous reaction products, evaporating water from the reaction medium and depositing solid reaction products in the reaction vessel, first conduit means in communication with the base of the vessel to conduct a slurry of deposited solid reaction product and reaction medium from the base, filtration means in communication with the first conduit means to remove part of the solid material from the slurry, recycle conduit means in communication with the filtration means and the reaction vessel to recycle an aqueous liquid containing make-up quantities of reactants and residual quantities of the deposited solid material to the reaction vessel, and heating means located in the recycle conduit means between the filtration means and the reaction vessel to heat the aqueous liquid, the improvement wherein the recycle conduit means terminates in the reaction vessel at a height therein above the maximum intended height of the reaction medium, and the recycle conduit means between the heating means and the reaction vessel includes a first frusto-conical portion of decreasing cross-sectional area in the direction towards the reaction vessel terminating at its downstream end in a collar, the first frusto-conical portion having a length sufficient to establish a back pressure exceeding the difference in

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saturation vapour pressure of heated aqueous liquid and of the reaction medium, and a second frusto-conical portion of increasing cross-sectional area away from the collar and terminating at its downstream end in a pipe, the second frusto-conical portion being dimensioned to allow gaseous material to expand therein at low acceleration, the pipe being continuously curved, having a substantially uniform diameter along its length and terminating at its downstream end in the reaction vessel.

10   Generally, the sulphuric acid is added to the recycled liquid containing residual amounts of solid material

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as well as make-up amounts of sodium chlorate and reducing

agent downstream of the heat exchanger. To prevent the

formation of local "hot spots" upon dilution of the acid it

is usual to employ sulphuric acid which has been diluted to

approximately 50% w/w. The present invention enables sub-

stantially concentrated sulphuric acid to be used without

formation of hot spots.

The invention is illustrated by the accompanying

drawings, in which:

Figure 1 is a schematic representation of a reactor

modified in accordance with one embodiment of the invention;

and

Figure 2 is a close-up view of part of the

apparatus of Figure 1.

In the drawings, a chlorine dioxide generator

vessel 10 of diameter D_o contains a reaction medium 12 which

is aqueous sodium chlorate, sodium chloride and sulphuric acid

maintained at its boiling point under a reduced pressure. A

mixture of sodium chloride and hydrogen chloride may be used,

if desired, in which event the quantity of sulphuric acid

may be lowered, with the hydrogen chloride providing the

remainder of the acid. The quantity of sodium sulphate produced

per unit of chlorine dioxide thereby is reduced. The hydrogen

chloride may be used to provide all the reducing agent and

up to half the acid requirement. Chlorine dioxide, chlorine

and water vapour are formed and are removed from the generator

10 as a gaseous mixture by line 14. The chlorine dioxide may

be recovered from the gaseous mixture in any convenient

manner.

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The liquid level 16 is maintained substantially constant during chlorine dioxide production, by control of the evaporation of water from the reaction medium 12 and the addition of water with the make-up chemicals.

Sodium sulphate is deposited from the reaction medium 12 and a slurry of product sodium sulphate and reaction medium is withdrawn by line 18 from the generator 10. The form of the sodium sulphate depends on the reaction conditions in the reaction medium 12. Make-up quantities of aqueous solution of sodium chlorate and sodium chloride are added to the slurry by line 20 and solid sodium sulphate is removed from the resulting mixture by line 22 through pump 24.

The solution of sodium chlorate and sodium chloride containing some solid unremoved sodium sulphate remaining after removal of the solid material through line 22 is passed by line 26 through pump 28 and line 30 to a reboiler 32. In the reboiler 32 the solution is heated to the boiling point of the reaction medium 12 under the prevailing conditions of the generator 10 and is forwarded by line 34 to the generator 10. The point of entry of the feed from line 34 to the generator 10 is a distance h_3 (see Figure 2) above the liquid level 16 in the generator 10. The form of line 34 is illustrated in Figure 2 and described in more detail below. Sulphuric acid is fed by line 35 to the solution in line 34 so that chlorine dioxide begins to form in line 34 by reaction between the materials in this line.

As seen in detail in Figure 2, the line 34 includes a first frusto-conical portion 36 of length h_2 and of reducing cross-sectional area in the direction of flow of the

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liquor of flow rate Q_2 from a diameter D_3 at the reboiler and terminating in a collar 38 of diameter D_2. Sulphuric acid inlet tubes 40 in communication with line 35 are spaced around the collar 38. There are four such inlet tubes 40 provided in diametrically opposed pairs, the pairs being at right angles to each other. Any desired number and orientation of such inlet tubes may be provided. The collar generally is of short length sufficient only to allow the addition of sulphuric acid by inlet tubes 40.

A second frusto-conical portion 42 of length h_1 and of increasing cross-sectional area downstream from the collar 40 from a diameter D_2 at the collar 40 to diameter D_1. The second frusto-conical portion 42 terminates in a continuously curved pipe or elbow 44, which may be a five-section pipe, of substantially uniform diameter D_1 through which material flows at a rate Q_{MF}. The curved pipe 44 terminates at its downstream end in communication with an inlet flange 46 on the generator 10, the inlet flange 46 having a length L_1.

Thus, liquid leaving the reboiler 32 first is accelerated to a high velocity in the first frusto-conical portion 36 of the line 34. The first frusto-conical portion 36 is dimensioned so that the back pressure caused by the acceleration of the liquid in the first frusto-conical portion 36 exceeds the difference in saturation vapour pressure of the liquid present and of that of the generator 10. Preferably, the compression section length h_2 is approximately 2.5 times the diameter D_2. For the temperature rise designed for in the reboiler 32, the liquor height equivalent to the rise in saturation vapour pressure thereacross may be designated S.

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If it is assumed that there is no energy loss in the height h_2, then

$$S = \frac{V_w^2}{2g} - \frac{V_x^2}{2g} + h_2$$

where V_w is the velocity of the liquor in the collar 38 and V_x is the velocity of the liquor at the exit of the reboiler 32. But, $h_2 = 2.5 \, D_3$

and $\qquad V_x = \left(\frac{D_2}{D_3}\right)^2 V_w \qquad$, and hence

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$$S = \frac{V_w^2}{2g} - \frac{V_x^2}{2g} + 2.5 \, D_3$$

and, therefore, since S is known V_w may be calculated and thence diameter D_2.

In this way, boiling of recycling liquid in the boiler 32 is avoided and hence the possibility of clogging of the reboiler tubes with solid deposit is reduced. In effect, the first frusto-conical portion 36 of tube 34 acts in the same manner as the hydrostatic head above the recycle feed

20 in a conventional evaporator as described above.

The sulphuric acid in line 35 fed to the liquid in the coller 38 may be and preferably is concentrated (approximately 98%) sulphuric acid. This is in contrast to the prior art use of 50% w/w sulphuric acid. By utilizing a line 34 of the structure illustrated in Figure 2, it is possible to introduce high concentration sulphuric acid into the recycle liquid without the formation of "hot spots". The sulphuric acid is fed rapidly into the collar 38 through the inlet tubes 40. Due to the speed of motion of the liquid

30 in the collar 38 and the sulphuric acid, a rapid mixing of

the materials occurs in the liquid phase. The strong acid thus is added to the accelerated heated mixture substantially at its maximum velocity.

By using concentrated sulphuric acid, it is possible to avoid the use of the dilution techniques required in prior art operations to achieve a concentration of sulphuric acid of 50% w/w. Further, the quantity of water introduced into the system is reduced and hence the heat required to evaporate sufficient water to maintain the substantially constant liquid level 16 is reduced. Additionally, the full heat of dilution of the concentrated sulphuric acid is realized and hence a further thermal economy is effected.

The mixture then is expanded at the low acceleration in the second frusto-conical portion 42 of the line 34 so that boiling of the liquid and gaseous product release is brought about evenly and gradually.

Since the liquid commences to boil and chlorine dioxide starts to form in the collar 38, the material in the pipe 44 is mainly gaseous with amounts of liquid and solid suspended therein.

The velocity of the vapour/solid/liquid mixture in the pipe 44 is quite low, typically about 35 to 40 ft/sec. and hence as the liquid enters the generator 10 it does not impinge on the opposite wall of the generator, but rather discharges into the reaction medium 12. If it is assumed that there is no slip flow in the pipe 44 and a velocity of about 40 ft/sec. in the pipe 44 is utilized, then

$$\text{the velocity} = 40 = \frac{Q_{MF}}{\left(\frac{\pi D_1^2}{4}\right)} \text{, and thus:}$$

$$Q_{MF} = 31.41 \, D_1^2$$

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$(D_O + L_1)$ is the maximum length of horizontal
path of the material entering the generator 10 from the pipe
44 if there is no impingement of this material on the
generator wall, and

$(h_3 + D_1)$ is the maximum height of the trajectory
of the discharged material into the reaction medium 12.

Thus, $(h_3 + D_1) = \frac{1}{2} g t^2$

$\frac{(D_O + L_1)}{t} = 40$, and hence

$$\frac{h_3 + D_1}{16.1} = \left(\frac{D_O + L_1}{40}\right)^2$$

Hence, for any given set of conditions a minimum
value for D_O may be determined which permits the discharge
of a vapour/solid/liquid mixture from the pipe 44 into the
generator 10 without impingement of the material on the walls
of the generator 10. In actual practice, the simplification
of no-slip flow in the pipe 44 often does not occur and,
due to vapour separation in the pipe 44 and in the trajectory
into the generator 10, a value of 60% of the minimum diameter
D_O calculated from the above equation has been found
acceptable.

By allowing boiling of the liquid to develop
gradually in the second frusto-conical portion 42 while
maintaining acceleration at a low level, hydrostatic head
and flashing are balanced, thus vibration and high frictional
pressure drop are avoided. All the gaseous material is
assumed to be flashed from the liquor at the commencement
of pipe 44. The second frusto-conical section 42 should be
as long as possible to allow the gradual development of the
boiling of the liquid at low acceleration without causing

undue vibration, although layout considerations dictate the practical limits of length h_1.

Detailed mathematical relationships for the second frusto-conical section 42 are difficult to arrive at and require solution of the momentum equation over incremental lengths of the section 42:

$$-\Delta P = \frac{G_T^2}{2g} \left[2 \left(\frac{X_{g2}}{\rho_{g2}} - \frac{X_{g1}}{\rho_{g1}} \right) + \frac{4FL}{\rho_{(NS)} D} \right]$$

10   wherein $-\Delta P$ is the pressure drop across an incremental section, G_T is the total flow, X_{g2} is the fraction of vapour at the downstream end of the section 42 and X_{g1} is the fraction of vapour at the upstream end and ρ_{g2} and ρ_{g1} are the specific gravities at those locations, F is the fanning fraction factor, L is the length of the incremented section, D is the diameter and $\rho_{(NS)}$ is the specific gravity at the incremental section assuming no slip.

Typically, a minimum length of 4'6" is used where the volume of steam flashed off is around 4000 lbs/hr.

20   In a typical operation, the velocity of the liquid leaving the reboiler 32 is about 11 ft/sec., that in the collar 38 is about 15 to 16 ft/sec. and that in the pipe 44 is about 36 ft/sec.

In contrast, in a chlorine dioxide-producing operation omitting the line 34 of the form shown in Figure 2 but instead utilizing a conduit of uniform diameter, then due to flashing flow the velocity of the liquid in the feed conduit to the generator is about 100 ft/sec.

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Obviously, in the case where chlorine dioxide is produced by reaction of sodium chlorate with hydrochloric acid, as described in Canadian Patent No. 913,328 mentioned above, since the hydrochloric acid provides both the reducing agent and the acid source, make up quantities of sodium chlorate only are added by line 20, the reducing agent-acid source being added later by line 35.

It will be apparent, therefore, that the present invention provides a method and apparatus for chlorine dioxide production which is a substantial improvement over the art, reducing wear of generator walls, allowing the use of reboilers without causing undue vibration and allowing concentrated sulphuric acid to be employed as an additive.

Modifications are possible within the scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1.   A continuous method of producing chlorine dioxide which comprises continuously maintaining a chlorine dioxide-producing reaction medium in a reaction zone, the reaction medium containing an alkali metal chlorate, a reducing agent capable of reducing said alkali metal chlorate to chlorine dioxide and chlorine and a strong mineral acid, continuously generating chlorine dioxide and chlorine from said reaction medium and continuously evaporating water from said reaction medium at substantially the boiling point thereof while the reaction medium is maintained under a reduced pressure, continuously removing from said reaction zone a gaseous mixture consisting of said generated chlorine dioxide and chlorine and said evaporated water, continuously recovering chlorine dioxide from said gaseous mixture, continuously depositing in said reaction zone an alkali metal salt of the anion of said strong acid, continuously removing from said reaction zone a slurry containing deposited alkali metal salt and part of said reaction medium, continuously forming a recycle mixture having a reduced alkali metal salt solids content and containing make-up quantities of alkali metal chlorate and reducing agent, except that said reducing agent is omitted from said recycle mixture when said strong mineral acid also provides said reducing agent, heating said recycle mixture substantially to an elevated temperature which is the boiling point of said reaction medium at the prevailing absolute pressure in said reaction zone, accelerating the heated mixture to establish a back pressure exceeding the difference in saturation vapour pressure of the heated mixture and of said reaction medium, adding strong mineral acid to said accelerated heated mixture substantially at the maximum velocity of said mixture resulting from said acceleration to provide a feed material for said reaction zone, allowing gaseous material in said feed material to expand while maintaining a low rate of

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acceleration, feeding said expanded feed mixture to said reaction zone at a level above the liquid level in said reaction zone, and maintaining the level of liquid in said reaction zone substantially constant.

2.   The method of claim 1 wherein said alkali metal chlorate is sodium chlorate.

3.   The method of claim 1 wherein said reaction medium contains sodium chlorate, sodium chloride and sulphuric acid.

4.   The method of claim 1 wherein said reaction medium contains sodium chlorate, hydrochloric acid and sulphuric acid.

5.   The method of claim 1 wherein said reaction medium contains sodium chlorate and hydrochloric acid.

6.   The method of claim 1 wherein said strong mineral acid is sulphuric acid and is added to said accelerated heated liquid in substantially concentrated form.
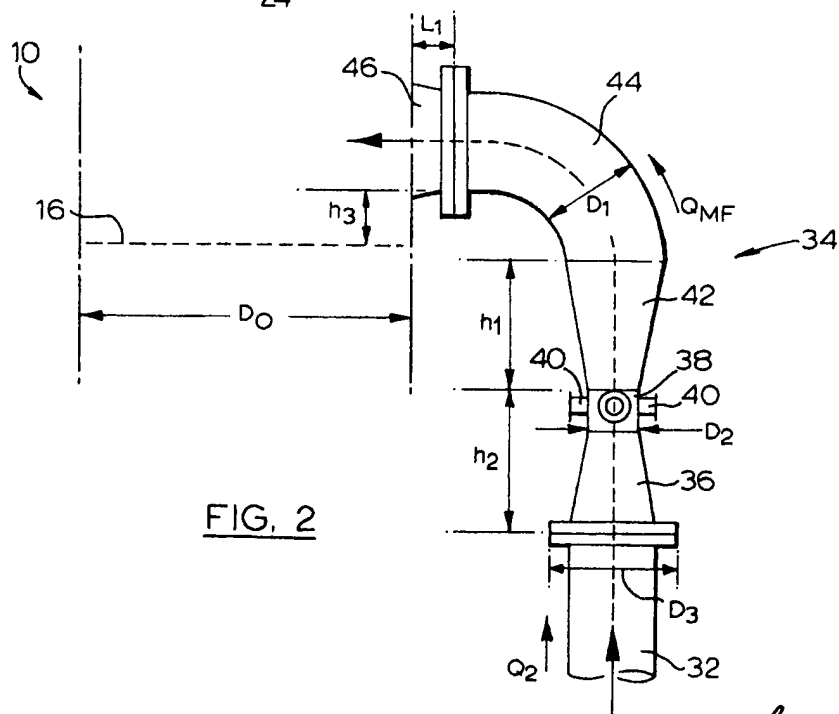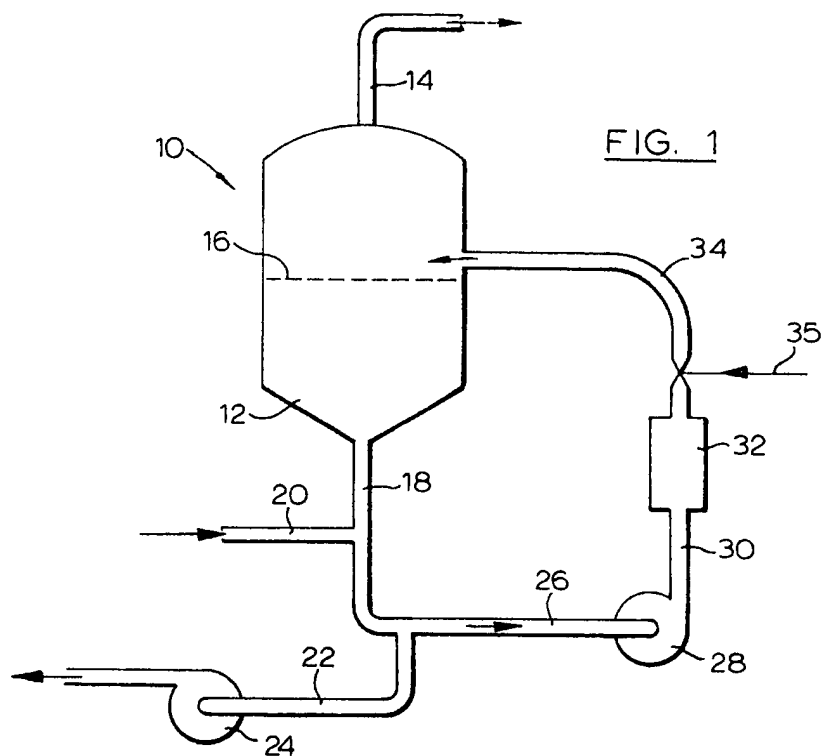
7.   In a gaseous reaction product generator comprising a reaction vessel adapted to hold an aqueous reaction medium and capable of forming gaseous reaction products, evaporating water from the reaction medium and depositing solid reaction products in the reaction vessel, first conduit means in communication with the base of said vessel to conduct a slurry of deposited solid reaction product and reaction medium from said base, filtration means in communication with said first conduit means to remove part of said solid material from said slurry, recycle conduit means in communication with said filtration means and said reaction vessel to recycle an aqueous liquid containing make-up

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quantities of reactants and residual quantities of said deposited solid material to said reaction vessel, and heating means located in said recycle conduit means between said filtration means and said reaction vessel to heat the aqueous liquid, the improvement wherein said recycle conduit means terminates in said reaction vessel at a height therein above the maximum intended height of the reaction medium, and said recycle conduit means between said heating means and said reaction vessel includes a first frusto-conical portion of decreasing cross-sectional area in the direction towards said reaction vessel terminating at its downstream end in a collar, said first frusto-conical portion having a length sufficient to establish a back pressure exceeding the difference in saturation vapour pressure of heated aqueous liquid and of the reaction medium, and a second frusto-conical portion of increasing cross-sectional area away from said collar and terminating at its downstream end in a pipe, said second frusto-conical portion being dimensioned to allow gaseous material to expand therein at low acceleration, said pipe being continuously curved, having a substantially uniform diameter along its length and terminating at its downstream end in said reaction vessel.

8.   The generator of claim 7 including further conduit means in fluid flow relationship with said collar.

9.   The generator of claim 8 including additional conduit means in fluid flow relationship with said first conduit means.

10.   The generator of claim 7 wherein the length of said first frusto-conical portion is about 2.5 times its diameter at its upstream end.

11.   The generator of claim 7 wherein said reaction vessel includes an upper right cylindrical portion and a conical base portion, said first conduit means extends down-

wardly substantially axially of the vessel from the substantial apex of said conical base portion, said recycle conduit means includes a first substantially horizontal portion extending from and in fluid flow communication with said first conduit means, a second substantially vertical portion extending substantially parallel to said first conduit means and terminating in said heater means and pump means situated between said first and second conduit portions, said first and second frusto-conical portions are located substantially in the vertical axis of said second conduit portion and said pipe terminates substantially radially of the right cylindrical portion of said vessel.

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FIG. 1

FIG. 2